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Magnetic and optical properties of WO_3/TiO_2 superlattice

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HIGHLIGHTS

- We found the magnetic phenomenon in the WO_3/TiO_2 thin film.
- The electrons transfer from TiO_2 and WO_3 induce the occurrence of ferromagnetism.
- The electrons transfer between TiO_2 and WO_3 shift the absorption region to visible light.

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ABSTRACT

The electronic structure and properties of WO_3/TiO_2 superlattice were investigated by the calculation and experiment. The O electrons transfer the spin angular momentum from the unoccupied Ti e_g states electrons to W e_g states electrons and let Ti and W electrons spin splitting, which were the reason of ferromagnetism occurrence, while the electrons transfer from the CB of TiO_2 to the CB of WO_3. Coupling TiO_2 and WO_3 greatly reduce the recombination rate of electron and hole and shift the absorption region to visible light because of the electrons transfer between TiO_2 and WO_3.

1. Introduction

Spuerlattices are materials with narrow-band-gap and wide-band-gap, which can improve the effective electron quantity and activity [1–3]. Coupling nanometer TiO_2 with narrow band gap semiconductor (CdS、MgO、WO_3、Fe_2O_3) may apparently improve the active of TiO_2 and induce the ferromagnetism occurrence. Researchers [4–6] have reported that coupled TiO_2 with WO_3 (WO_3/TiO_2) can decrease the photo-induced hole-electrons recombination rate and the light absorption region transfer to visible light. Coey's group [7] discovers the high-temperature ferromagnetism of HfO_2 thin film and firstly proposes the anisotropic high-temperature d^0 ferromagnetism. Yoon's group [8] finds that the oxygen vacancies surrounding Ti^{2+} and Ti^{3+} ions potentially can give rise to magnetism of $TiO_{2-\delta}$ films. The room-temperature ferromagnetism of $SmCo_5/Co$ films are induced by strong interaction of Sm and Co [9]. The Fe_2O_3/TiO_2 films [10] possess higher photocatalysis efficiency than pure TiO_2 films and the Fe_2O_3/TiO_2 composite particles [11] possess room-temperature ferromagnetism which comes mainly from Fe_2O_3 phase. Choi et al. [12] proved the existence of uniaxial magnetic anisotropy in epitaxial Fe/MgO films on GaAs (001).

However, the superlattice materials all have magnetic phases and it is of great significance to develop new type superlattice magnetic materials. Herein, we investigated the micro-structure, optical and magnetic properties of WO_3/TiO_2 thin films by the coupling method of experiment and calculation. We found the ferromagnetism of WO_3/TiO_2 thin films and explain the occurrence reason of ferromagnetism.

2. Calculations and experiments

The calculation method of pure TiO_2 and WO_3/TiO_2 superlattice are consistence with the calculation method described in Ref. [13], but the parameter setting is not exactly same. The CASTEP code was used to calculation, the electron wave function was expanded in plane waves up to cut-off energy of 450 eV. The Monkhorst-Pack scheme k-points grid sampling was set to be $4 \times 4 \times 5$ for the

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Table 1
The band gap of anatase TiO_2 and WO_3 with different U values.

U (eV)	0.00	3.00	5.00	7.00	8.00	8.50	9.00
Eg of TiO_2 (eV)	2.14	2.55	2.83	3.05	3.18	3.22	3.29
Eg of WO_3 (eV)	1.48	2.08	2.47	2.71	2.84		

unit cell and $8 \times 8 \times 10$ for the supercell. As displayed in Table 1, the U = 8.50 eV for Ti 3d and U = 7.00 eV for W 5d were selected in subsequent calculations, because of the bandgap of TiO_2 and WO_3 were 3.22 eV and 2.71 eV, respectively, which is consistent with the experiment ones [14,15].

The $2 \times 2 \times 1$ superlattice of TiO2 was built (Fig. 1a) for pure TiO_2 calculation. The lattice plane of TiO_2 and WO_3 were (002) and (101) respectively, in the WO_3/TiO_2 crystal model [6]. As shown in Fig. 1, the crystal model b, c and d were named W_4T_4、W_4T_6 and W_4T_8, respectively, because of the atom number of the W and Ti. The a, b, α, β, γ of W_4T_4、W_4T_6 and W_4T_8 are the same, and a = 0.536028 nm, b = 0.446862 nm, α = β = 90.0000°, γ = 100.148°, but c of W_4T_4、W_4T_6 and W_4T_8 are different, c = 1.48067 nm for W_4T_4, c = 1.83149 nm for W_4T_6, c = 2.26029 nm for W_4T_8. All the models were geometrically optimized, then total density of states (TDOS) and partial density of states (PDOS) were calculated and analyzed.

The WO_3/TiO_2 thin films were prepared by magnetron sputtering method. At firstly, spurting Ti on 3 sheets cleaned ultraviolet quartz glasses for 15 min, then the sheet glasses with coating were calcined at 500 °C for 0.5 h. Secondly, spurting W on the glasses with coating for 5 min, 10 min and 15 min, respectively. Then the glasses were calcined at 500 °C for 0.5 h. The WO_3/TiO_2 thin films based on silicon slices were prepared by the same method. The WO_3/TiO_2 thin films were named W_5T_{15}, $W_{10}T_{15}$ and $W_{15}T_{15}$ because of the W and Ti spurting time, respectively.

The crystallite phases of the samples were identified by XRD on X'pert Philips using Cu Kα (λ = 0.15406 nm) radiation operating at 40 kV and 30 mA at a rate of 0.03°/s. The diffraction data were recorded between 15° and 80°. The magnetic properties of WO_3/TiO_2 were characterized by VSM (Versalab, Quantum DeSign, USA) at room temperature. The absorption spectra were determined by spectroscopic analysis at 508 nm using a UV spectrometer (UV-1801, China).

3. Results and discussion

According to the crystal field theory, due to the hybridization of Ti—O and W—O, the Ti 3d and W 5d orbits split into two parts, the t_{2g} (d_{xy}, d_{xz}, d_{yz}) and e_g (d_{z^2}, $d_{x^2-y^2}$) states, meanwhile the O 2p orbit split into p_π and p_s states. O 2p and the t_{2g} (d_{xz}, d_{yz}) of Ti 3d and W 5d devoted to the valence band (VB) (p_π devote to the top of valance band), while the conduction band (CB) was contributed by the d_{xy} and e_g of Ti 3d and W 5d (d_{xy} devote to the bottom of conduction band) [16]. Fig. 2 shows the TDOS and PDOS of TiO_2 and the TDOS and PDOS of WO_3/TiO_2, respectively. Comparing with pure TiO_2 (3.22 eV), the W_4T_4 (1.45 eV) and W_4T_6 (0.62 eV) have more narrow band gap, and the W_4T_8 has not obviously forbidden band. These illustrate that coupling TiO_2 with WO_3 can decrease the energy required for electron transfer and shift the light absorption region from ultraviolet to visible light.

As shown in Fig. 2a, there is no splitting between the spin-up and spin-down states, which confirms that TiO_2 has not magnetism. For the TDOS of WO_3/TiO_2 (Fig. 2b (I), c (I) and d (I)), there is a spin-split around the Fermi Level illustrating the existence of magnetism. For the PDOS of W 5d, O 2p and Ti 3d (Fig. 2b (II, III and IV), 2c (II, III and IV), 2d (II, III and IV)), there are also exchange splitting around the Fermi level between the spin-up and spin-down states, and the magnetic moment was mainly devoted by W and Ti atoms. The bottom of CB (d_{xy}) move to a low energy region and the top of VB (p_π) move to a high energy region with the increasing of TiO_2. This is the reason of why there is not obviously forbidden band in W_4T_8.

The XRD patterns for the pure and coextruded films are displayed in Fig. 3. The diffraction peaks of each sample can be indexed to anatase phase with space group $I4_1/amd$ (141) and the tungsten oxide phase with space group P21/n and P4/nmm, which indicate that the W has not complete oxidation in $W_{10}T_{15}$ and $W_{15}T_{15}$ samples for calcined 0.5 h.

Researchers [17–19] found the ferromagnetism of TiO_2 films and indicated that the ferromagnetism of TiO_2 thin films were

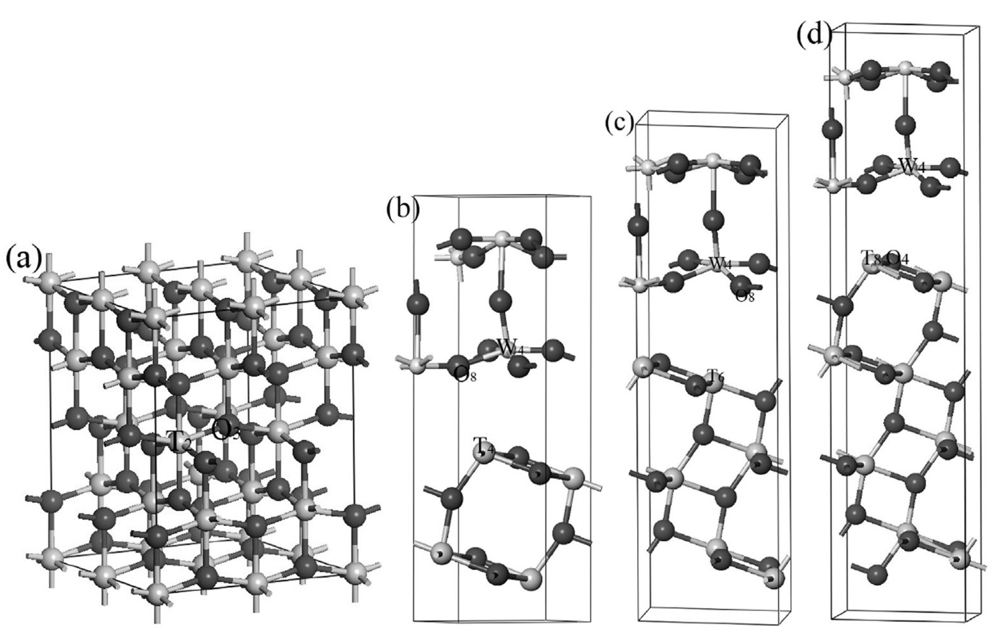

Fig. 1. The $2 \times 2 \times 1$ superlattice model of TiO_2(a) and superlattice crystal model of WO_3/TiO_2. The number ratio of W and Ti atoms were 4:4 (b), 4:6 (c), 4:8 (d).